APPLICATIONS OF EXCHANGE ADSORBENTS

I. PREPARATION OF LEVULOSE SIRUPS

II. REACTIONS WITH AMINO ACIDS

BY

HAROLD ALVIN FIESS

B.S., Wheaton College, 1939

M.S., University of Illinois, 1942

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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APPLICATIONS OF EXCHANGE ADSORBENTS

I. Preparation of Levulose Sirups

Introduction

The production of a palatable sirup by direct hydrolysis of an aqueous extract of inulin containing materials, as the Jerusalem artichoke, has been a subject for investigation at the University of Illinois. Various processes of manufacture have been developed but one of the most promising from the standpoints of expense and of palatability of the finished product has involved the use of synthetic ion-exchange materials (1) (2). Cation exchangers such as sulfonated coal or phenol formaldehyde resins are acidic and the hydrogen ion can be reversibly exchanged for cations. Insoluble basic amine exchangers reversibly adsorb acid molecules from solution (3). The cation exchangers, when allowed to react with the artichoke extracts, were effective in exchanging hydrogen ions for potassium and other ions, thus increasing the acidity to a value adequate for hydrolysis and simultaneously decreasing the ash content of the extract. After hydrolysis, neutralization was accomplished by the removal of organic and inorganic acids with the anion exchangers.

This investigation was undertaken; (a) to study further the reaction between the exchangers and the aqueous artichoke extract; (b) to devise a good commercial procedure; and (c) to apply the method to other levulose yielding plant materials.

Experimental and Results

In commercial practice exchange is usually effected by allowing a solution to percolate through a bed or column of exchanger. Column exchange treatment of artichoke extracts was found to be impossible due to clogging of the bed. The colloidal impurities responsible for this action were found to be removable in part through preliminary acidification to the flocculation point prior to column exchange. Pre-clarification of the extracts facilitated column flow but did not insure complete success. On the other hand column anion exchange was possible in all cases.

A counter-current batch procedure was then developed as a substitute for column cation exchange. Employing a series of

cells of exchange material a quantity of extract was passed through the cells and exchange effected in a series of steps. When a portion of the extract had passed through the battery of cells, the pH of the extract was lowered to a minimum value and simultaneously one cell was exhausted in capacity. This procedure was found to be very satisfactory for cation-exchange treatment of all inulin containing extracts. Data were obtained demonstrating the acceptable performance of the counter-current batch procedure.

Flocculated impurities of aqueous artichoke extracts, although bulky, represented only five per cent of the total nitrogen constituents. However in the process of exchange nearly all this fraction was removed by chemical combination or by strong physical adsorption. The cation exchanger was much more effective in removal of the nitrogen fraction than was the anion exchanger although both were active.

The production of palatable sirups by the ion exchange process from a number of levulose containing tubers was studied. Using the artichoke as a source of raw material in the forms of the sliced fresh tuber, the sliced dried tuber, flour, and purée, highly palatable sirups were prepared. The extraction process must be modified since it depends upon the form of raw material. From a number of points of view the sliced dried material is the easiest to process.

A palatable sirup was prepared from sliced dried dahlia tubers. Previous attempts to prepare a palatable sirup from chicory tubers were unsuccessful because of the presence of bitter constituents. Removal of these bitter components was effected when the aqueous extract was allowed to react with the exchangers. The resultant chicory sirup was palatable.

II. Reactions with Amino Acids

The observation that the nitrogen fraction of aqueous artichoke extracts reacted with ion-exchange adsorbents prompted a study of the reaction of amino acids with the exchangers. In this investigation, the mechanism of reaction was determined after collection of a large amount of analytical data. The study included observations on the reactions of the exchange materials with individual amino acids with an aim toward chromatographic separation of two or more components.

Experimental and Results

The exchange materials were prepared by screening to —20 +40 mesh, activating with the proper reagents, and air-drying under comparable conditions. The commercial exchangers, Zeo-Karb H, Amberlite IR-1, and Amberlite IR-100, were used for cation exchange; Amberlite IR-4 and De-Acidite were used for anion exchange. Two quantitative methods for examination of base-exchange reactions were used. One method termed column exchange or dynamic exchange is based on the examination of the solution that percolates through a bed of exchange material by gravity flow. Static exchange, analogous to the batch procedure involves contact between the exchanger and the solution until equilibrium is attained.

For the examination of dilute solutions of amino acids a colorimetric procedure based upon the reaction with sodium β-naphthoquinone-4-sulfonate was selected.

All the amino acids tested were found to react with the hydrogen form of the cation exchangers. Using the column method, the capacities of two commercial exchangers, Amberlite IR-1 and Zeo-Karb H, for glycine, leucine, norleucine, phenylalanine, tryptophane, hydroxyproline, glutamic acid, asparagin, and lysine hydrochloride have been determined. Apparently the removal of amino acids from solution proceeds by salt formation between the basic amino group and the acid form of the exchanger. This conclusion was substantiated by the fact that static studies of the adsorption of glycine from solutions containing varying amounts of HCl showed decreasing removal as the pH was lowered. Still further evidence for this conclusion is furnished by the fact that the calcium and sodium forms of the cation exchangers either did not react or reacted very slightly with amino acids.

Addition of formaldehyde to the amino acid solutions had little effect upon their reaction with the hydrogen form of the exchangers.

Adsorption of the nine amino acids by the hydrogen exchangers was studied by static methods also. Previously used equations for treating the data were not found to be entirely applicable.

The anion exchangers were found to react with monoamino

dicarboxylic acids but not with the monoamino monocarboxylic acids. Thus a quantitative separation of these two groups of acids may be accomplished. The basic amino acid hydrochlorides were not removed by the anion exchangers.

A study of the adsorption of the two amino acids in the presence of each other showed a modification of the adsorption curves, resulting in a decrease in adsorption of the amino acid that is normally least adsorbed and an increase in adsorption of the amino acid that is normally more strongly adsorbed. This action occurs with both exchangers but is greater in Amberlite IR-1.

Complete quantitative separation of tryptophane from asparagin indicated the possibility of separation of the aromatic amino acids from the aliphatic amino acids and is in accord with the observations of Schramm and Primosigh (4) obtained with activated carbon.

Partial separation of glycine and glutamic acid, and hydroxyproline and leucine indicates that further investigation will show that separations of other amino acids may be possible.

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VITA

The author was born in Ringoes, New Jersey, April 28, 1917. He attended the Ringoes grammar school until 1930 and graduated from the Flemington High School in 1934. His undergraduate work was done at Wheaton College, Wheaton, Illinois, where he received the degree of Bachelor of Science in 1939. From September, 1937 to June, 1939 he was an undergraduate assistant in the Chemistry Department of Wheaton College. From September, 1939 to August, 1940, he held the position of chemist with the American Cyanamid and Chemical Co., Woodbridge, New Jersey. In September, 1940 he matriculated at the University of Illinois and in February, 1942 he received the degree of Master of Science in Chemistry from that institution. He held a teaching assistantship in the Chemistry Department at the University of Illinois from September, 1940 until June, 1943, and a University Fellowship from June, 1943 to February, 1944. During the Summer of 1942 he was a Special Research Assistant for the National Defense Research Committee. He is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Sigma Pi Sigma. He is co-author of the following publication:

Englis, D. T., and Fiess, H. A., "Production of a Palatable Artichoke Sirup—Application of Organic Exchangers," Ind. Eng. Chem., **34**, 864 (1942).

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